Classification of Ligands: II
The L, X, Z approach

Malcolm Green : The CBC Method for Covalent Bond Classification used extensively in organometallic chemistry.

L ligands are derived from charge-neutral precursors: NH_3, amines, N-heterocycles such as pyridine, PR_3, CO, alkenes etc.

X ligands are derived from anionic precursors: halides, hydroxide, alkoxide alkyls—species that are one-electron neutral ligands, but two electron donors as anionic ligands. $EDTA^{4-}$ is classified as an L_2X_4 ligand, features four anions and two neutral donor sites. C_5H_5 is classified an L_2X ligand.

Z ligands are RARE. They accept two electrons **from** the metal center. They donate none. The “ligand” is a Lewis Acid that accepts electrons rather than the Lewis Bases of the X and L ligands that donate electrons.

Electron Counting for simple molecules

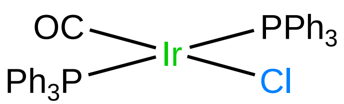
Whenever you see a metal complex, work out:

(a) Metal oxidation state (organic chemistry knowledge will help assign the correct charges to the ligands).

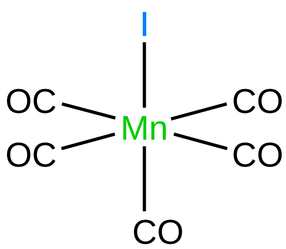
(b) d^n Electron configuration (remember, all valence electrons are d-electrons)

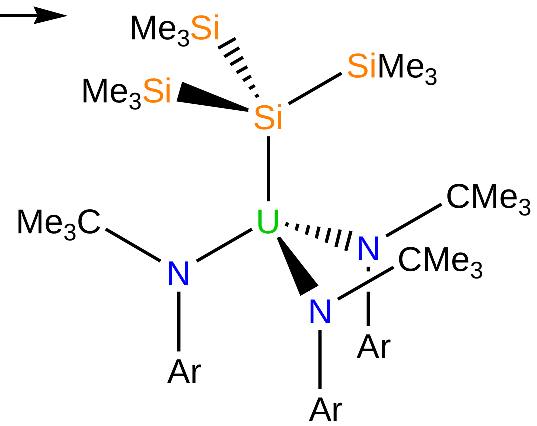
(c) Electron count for the complex

Chris Cummins (MIT) →



(Vaska's compound)





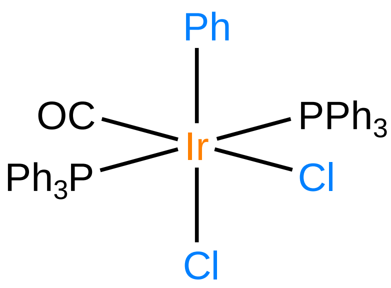
$Ir^+ = d^8$
$Cl^- = 2$
$2 \times PPh_3 = 2 \times 2 = 4$
$CO = 2$
Total = 16

$Mn^+ = d^6$
$I^- = 2$
$5 \times CO = 5 \times 2 = 10$
Total = 18

$Hg^{2+} = d^{10}$
$Br^- = 2$
$Me^- = 2$
Total = 14

$U^{4+} = d/f^2$
$3 \times NR_2^- = 3 \times 2 = 6$
$SiR_3^- = 2$
Total = 10

Alternative methods for electron counting



Method A
assign charge to metal

Ir^{3+} = d^6
2 x Cl^- = 2 x 2 = 4
Ph^- = 2
2 x PPh_3 = 2 x 2 = 4
CO = 2
Total = 18

Au^+ = d^{10}
2 x CN^- = 2 x 2 = 4
Total = 14

Method B
ligands and metal neutral

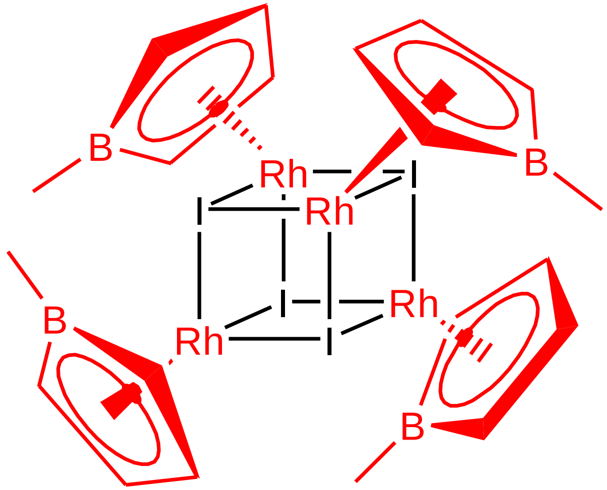
Ir = d^9
2 x Cl = 2 x 1 = 2
Ph = 1
2 x PPh_3 = 2 x 2 = 4
CO = 2
Total = 18

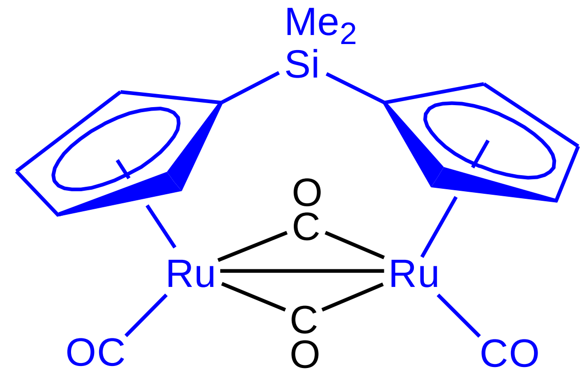
Au = 11 electrons
2 x CN = 2 x 1 = 2
1- charge = 1
Total = 14

- PH generally recommends this method, though sometimes problems exist

IMPORTANT: whichever method you use, be consistent !!!

Electron Counting Practice – Examples





Borole = dianionic version of Cp^-

Q = How should the μ_3-I^- ligands be counted ?

$SiMe_2(C_5H_4)_2^{2-}$ is just two Cp^- anions joined together

Q = How should the Ru-Ru bond be counted ?

Q = how should the bridging carbonyls be counted ?